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## **CLAIMS**

- 1. A method of case hardening an article of titanium or a titanium-based alloy, or of zirconium or a zirconium-based alloy, wherein the article is heat treated for a period of at least 12 hours at one or more temperatures in the range of 850°C to 900°C and at a pressure in the order of atmospheric pressure in an oxygen diffusion atmosphere comprising
  - a) a carrier gas which does not react chemically with the article in the said temperature range and
  - b) molecular oxygen, wherein the concentration of oxygen in the oxygen diffusion atmosphere is in the range of 10 volumes per million to 400 volumes per million.
- 2. A method as claimed in claim 1, in which the oxygen concentration is in the range of 75 to 300 volumes per million.
- 3. A method as claimed in claim 2, in which the oxygen concentration is in the range of 100 to 200 volumes per million.
- 4. A method according to any one of the preceding claims, in which the case hardened article is subjected to a further heat treatment at a temperature in the range of 500 to 900°C in an atmosphere having an oxygen concentration of at least 5000 volumes per million so as to form a visible surface oxide layer on the article that improves its tribological properties.
- 5. A method as claimed in claim 4, in which the atmosphere in which the tribological surface oxide layer is formed contains from 15 to 25% by volume of oxygen and from 75 to 85% by volume of argon.

- 6. A method as claimed in any one of the preceding claims, in which the said carrier gas is argon.
- 7. A case hardened article of titanium or a titanium-based alloy or of zirconium or a zirconium-based alloy obtainable by a method according to any one of the preceding claims.